Vol. 13 August 1937 No. 8

Bulletin of the Agricultural Chemical Society of Japan.

ABSTRACTS

from

TRANSACTIONS published in JAPANESE

(Pages refer to the Japanese originals of this volume unless otherwise noticed)

Studies on "Funasushi," Pickles of Crucian in Boiled Rice.

(pp. 635～638)

By Kenji MATSUSHITA.

(Agr. Chemical Laboratory, Kyoto Imperial University, and Kurita School of Agriculture, Shiga, Japan; Received May 27, 1937.)

Part II.—Isolation of lactic acid bacteria from "Funasushi."

Four strains of lactic acid bacteria were isolated from various stages of Funasushi, and these organisms were found to be streptococcus facium, Lactobacillus plantarum and two strains of Lactobacillus pentoaceticus.

Influence of Deficiency of Three Essential Elements (N.P.K) on the Yield, Ash-constituents (Si, Ca, P) and Nitrogen Content of Unhulled Rice.

About the Relations of the Typhoon of September 21, 1934.

(pp. 639～648)

By Chikafumi ICHIKAWA.

(The Soma Agricultural and Sericicultural School; Received May 28, 1937.)

On the Retting of some Vegetable-Fibre-Materials. (Part I.)

The Selection of Effective Micro-organism for the Bacterial Retting of the Ramie-Fibre-Materials.

(pp. 649～653)

By Toshio NAKAHAMA and Schunichi NISHIMURA.

(Chemical Laboratory, Kanebo Hikone Factory; Received May 29, 1937.)

Fifteen different micro-organisms were separated from some vegetable-fibre-materials and their cultural characteristics were studied.

After the ramie-fibre-materials were retted by the pure culture of each organism, the pectin contents of them were measured and the most effective one (Ram. F.) was selected.

On the Retting of some Vegetable-Fibre-Materials. (Part II.)

The Action of Ram. F. on the Retting of the Ramie-Fibre-Materials.

(pp. 654～656)

By Toshio NAKAHAMA and Schunichi NISHIMURA.

(Chemical Laboratory, Kanebo Hikone Factory; Received May 29, 1937.)

It was observed that quantities of pectin, hemicellulose and lignin were removed from the ramie-fibre-materials by the bacterial retting with Ram. F.

On the Retting of some Vegetable-Fibre-Materials. (Part III.)

On the Result of the Retting of the Ramie-Fibre-Materials with Ram. F.

(pp. 657～659)

By Toshio NAKAHAMA and Schunichi NISHIMURA.

(Chemical Laboratory, Kanebo Hikone Factory; Received May 29, 1937.)

The result of the retting of the ramie-fibre-materials with Ram. F. showed the yield and quality of the products to be generally good.

Polysaccharide X.

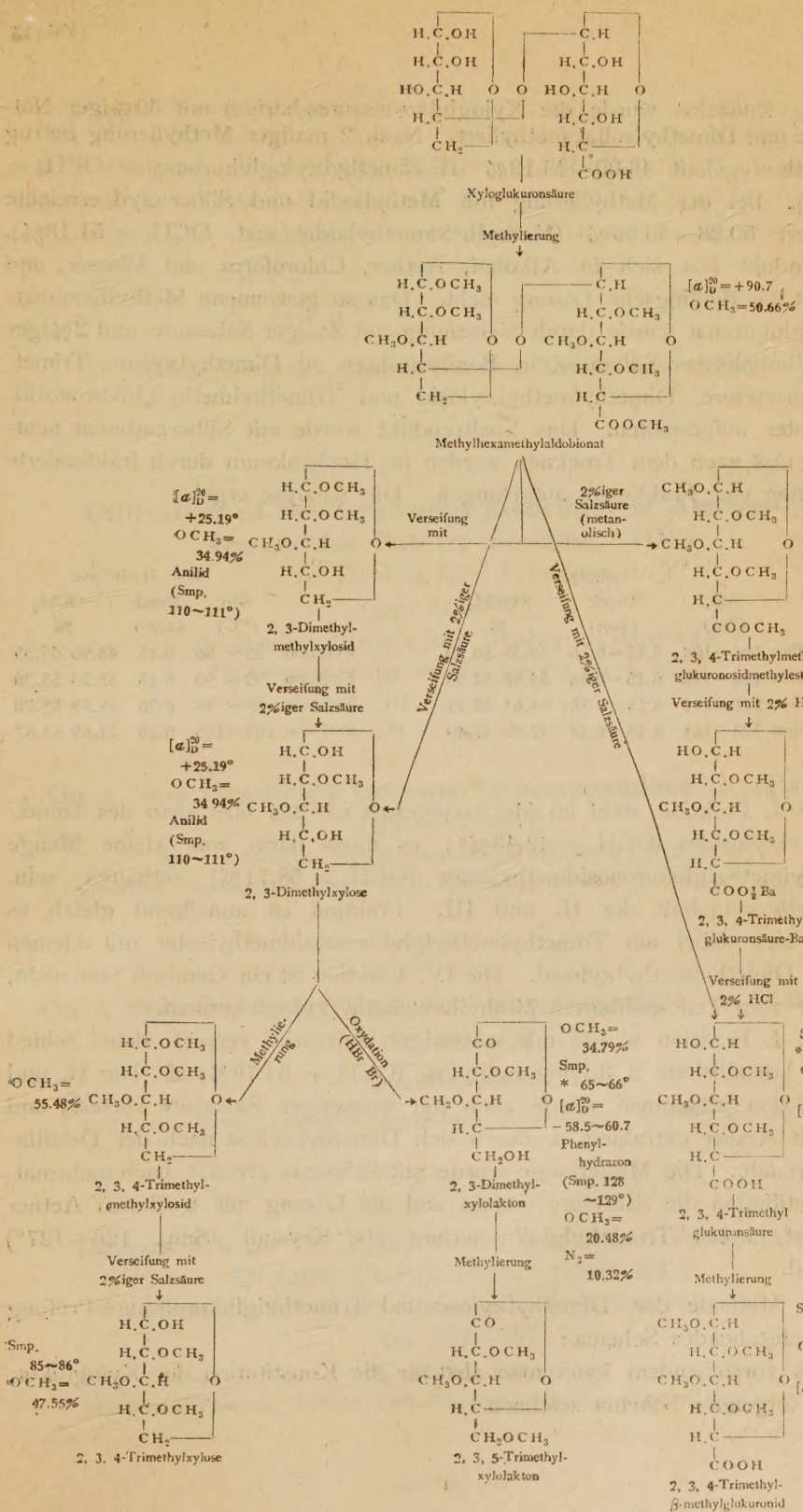
Ueber die Konstitution des neuen Disaccharids "Xyloglukuronsäure" aus Kadsura japonica, Don.

(SS. 660～672)

Von K. NISHIDA und H. HASHIMA.

(Holzchemisches Institut, Kyushu Kaiserliche Universität, Fukuoka, Japan; Eingegangen am 3, 6, 1937.)

Der Methylierungsversuch gibt Aufklärung über das Konstitutionsproblem des Disaccharids und wird somit durch ihn ein gewisser eindeutiger Abschluss


Xyloglukuronsäure
Methylierung
$[\alpha]_D^{20}$ = +90.7
OCH3 = 50.66%
Methylhexamethylaldobionat
Verseifung mit
2%iger Salzsäure (metanolisch)
$[\alpha]_D^{20}$ = +25.19°
OCH3 = 34.94%
Anilid (Smp. 110~111°)
2, 3-Dimethylmethylxylosid
Verseifung mit 2%iger Salzsäure
2, 3-Dimethylxylose
2, 3, 4-Trimethylmethylglukuronosidmethylester
Verseifung mit 2% HCl
2, 3, 4-Trimethylglukuronsäure-Ba
Verseifung mit 2% HCl
Methylierung
Oxydation (HBr Br)
OCH3 = 55.48%
2, 3, 4-Trimethylmethylxylosid
Verseifung mit 2%iger Salzsäure
Smp. 85~86°
OCH3 = 47.55%
2, 3, 4-Trimethylxylose
OCH3 = 34.79%
Smp. * 65~66°
$[\alpha]_D^{20}$ = −58.5~60.7
Phenylhydrazon (Smp. 128~129°)
OCH3 = 20.48%
N2 = 10.32%
2, 3-Dimethylxylolakton
Methylierung
2, 3, 5-Trimethylxylolakton
Smp. * 126~127°
OCH3 = 38.51%
$[\alpha]_D^{20}$ = 76.95~66.48
2, 3, 4-Trimethylglukuronsäure
Methylierung
Smp. 135~137°
OCH3 = 47.73%
$[\alpha]_D^{20}$ = −34
2, 3, 4-Trimethyl-β-methylglukuronid

erreicht. Zunächst wurde die Xyloglukuronsäures-barium mit 30%iger Natronlauge und Dimethylsulfat methyliert. Nach 2 maliger Methylierung betrug der Methoxygehalt 46.00~46.19% (Hexamethylxyloglukuronsäure OCH_3 = 45.37%). Bei der Methylierung mit Methyljodid und Silberoxyd erreichte der Wert 50.28~50.66% (Methylhexamethylaldobionat OCH_3 = 51.18%). Das Produkt löst sich in Alkohol, Aether, Chloroform und Wasser, und reduziert die Fehlingsche Lösung nicht. Das so gewonnene Methylhexamethylxyloglukuronat wurde durch Verseifung mit 2%iger Salzsäure und 2%iger methylalkoholischer Salzsäure in Bombenröhren zu Dimethylxylose, Trimethylglukuronsäure, Dimethylmethylxylosid und Trimethylmethylglukuronosidmethylester aufgespalten. Das Spaltprodukt wurde mit Silberkarbonat neutralisiert, und nach dem Trocknen werden im Hochvakuum durch fraktionierte Destillation vier Fraktionen aufgefangen. Die Analyse ergab.

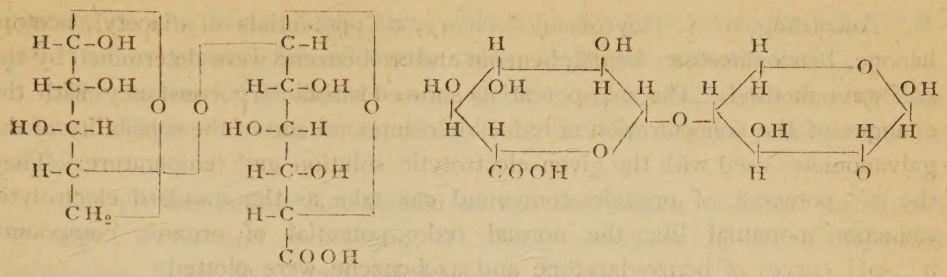
	I. Hydrolyse					II. Hydrolyse				
		Sdp. (°m)	Druck (mm)	OCH_3 %			Sdp. (°C)	Druck (mm)	OCH_3 %	
I.	Fraktion	104~108	0.15~0.16	50.35	50.29	I. Fraktion	85~ 86	0.15	48.96	49.35
II.	Fraktion	104~110	0.15~0.16	54.90	54.90	II. Fraktion	92~ 93	0.15	55.23	55.30
III.	Fraktion	111~114	0.15~0.16	54.61	54.71	III. Fraktion	97~ 98	0.20	55.89	55.78
IV.	Fraktion	120~165	0.15~0.18	47.99	47.49	IV. Fraktion	102~105	0.20	51.69	51.67

Die I. Fraktion steht im Methoxylgehalt ca. 2% über dem des Dimethylmethylxylosides (OCH_3 = 48.43%); es muss darin eine kleine Menge Trimethylmethylglukuronosidmethylester (OCH_3 = 58.71%) enthalten sein. Der Methoxylgehalt der II. und III. Fraktion ist annährend gleich, es handelt sich dabei um Trimethylmethylglukuronosidmethylester mit kleinen Mengen Dimethylmethylxylosid. Die IV. Fraktion ist ein Gemisch von nicht, oder nur zum Teil spaltbarem Methylhexamethylxyloglukuronat.

Die I. Fraktion wurde mit wässeriger Salzsäure verseift, dabei schied sich die kristallisierte 2, 3-Dimethylxylose (OCH_3 = 34.79%) ab. Die II. und III. Fraktion zusammen wurde auch mit wässeriger Salzsäure verseift, und dann mit Aether extrahiert, wodurch sich Dimethylxylose nach der Destillation abtrennte. Die Mutterlauge wurde mit Salzsäure versetzt, nach mehrmaliger Destillation die Salzsäure verjagt und die Lösung mit trocknem Aether extrahiert, wobei Trimethylglukuronsäure als Krystall (Smp. 126~127°) ausschied.

Die Methode der Dimethylxylose- und Trimethylglukuronsäure-Prüfung zeigt nachstehendes Schema:

Aus vorstehendem kann man also für die Konstitution der Xyloglukuronsäure folgendes Schema zeichnen.



(Holzchemisches Institut, Kaiserl. Kyushu-Universität)

Utilization of the Irradiated Mycelium of Aspergillus Oryzae for Poultry Feeding. (IV.)

Addition of Rice Polishings.

By Ryohei TAKATA and Kisaburo YOKOYAMA.

(The Osaka Imperial University; Received June 5, 1937.)

On a New Oxydising Enzyme "Sucro-oxydase". (Part I.)

By Toyosaku MINAGAWA and Junnosuke ICHIHARA.

(Agricultural Chemical Laboratory, Tokyo Imperial University; Received June 14, 1937.)

On a New Oxydising Enzyme "Sucro-oxydase". (Part II.)

By Toyosaku MINAGAWA.

(Agricultural Chemical Laboratory, Tokyo Imperial University; Received June 14, 1937.)

Researches on the Electrolytic Reduction Potentials of Organic Compounds. (Part 24.)

Consideration of the Electrolytic Reduction Potential.

By Isamu TACHI.

(Agricultural Chemical Institute, Kyoto Imperial University; Received June 21, 1937.)

According to J. Heyrovskij's theory, $\pi^1/_2$-potentials of diacetyl, acetophenone, benzoylacetone benzil, benzoin and azobenzene were determined by the half wave method. The $\pi^1/_2$-potentials showed satisfactory constancy with the changes of the concentration of reducible compound and of the sensibility of the galvanometer used with the given electrolytic solution and temperature. Then the $\pi^1/_2$-potential of organic compound can take as the standard electrolytic reduction potential like the normal redox-potential of organic compound. $\pi^1/_2$-pH curves of benzoylacetone and azobenzene were plotted.

Researches on the Electrolytic Reduction Potentials of Organic Compounds. (Part 25.)

Standard Electrolytic Reduction Potential and Redox-potential.

(pp. 698～704)

By Isamu TACHI.

(Agricultural Chemical Institute, Kyoto Imperial University; Received June 21, 1937.)

The electrolytic reduction of neutral red was investigated by the polarographic method.

The half wave potentials ($\pi^1/_2$) of neutral red in a given pH solution showed a constant value independently of the change of the concentration and of the sensibility of the galvanometer used. Then the $\pi^1/_2$-potential may be taken as a standard electrolytic reduction potential of neutral red. The standard electrolytic reduction potential (referred to normal hydrogen electrode) agreed with the redox-potential.

The number of hydrogen atoms related to the electrolytic reduction of neutral red were determined from the shift of the reduction potentials determined by the tangent method and were assumed to be 2 atoms.

The reduction potential -pH curves were given in the original paper.

On the Unsaponifiable Matter of the Alge Fats. III.

On the Toxic Components.

(pp. 705～709)

By K. SHIRAHAMA.

(Agr. Chemical Laboratory, Hokkaido Imperial University, Japan; Received June 16, 1937.)

K. Kawakami and I. Yamamoto* proposed to divide the toxic com-

* This Journ. **11** 400, (1935).

ponents of cod liver oil into three classes, i. e. "liver oil toxin "A" "B" and "C" or general fish oil toxin, cramp toxin and narcotic toxin.

The toxins of B and C come in the unsaponifiable fraction and the noxious effects are caused on albino rats by the way of subcutaneous injection.

The present author investigated on the distribution of these toxins in a few alge: leaves and sporophylls of *Alaria crassifolia Kjellm*, *Cystophyllum hakodatense Yendo* and *Laminaria ochotensis Miyabe*.

The unsaponifiable substances were separated from the alge fats, and after excluded sterols the liquid substances were extracted with 80% methanol. The quantities of the extracted substances were as follows:—

	Dry sub. of alge.	Unsaponif. matters.	Liquid sub. of unsaponif. fraction.	Ext. of 80% methanol
Alaria				
Leaves	40.5 kg	69 g	60 g	11.4
Sporophylls	15.5	8	5	0.5
Cytophyllum	27.0	40	22	8.0
Laminaria	20.0	14	12	0.6

0.25～0.50 g of those extracts were injected subcutaneously to the young albino rats. A characteristic cramp or narcotic effects were then caused on rats as shown in the following table.

	Amount of inject. sub.	Toxin	Time to death
Alaria			
Leaves	0.50 g	cramp	70 minutes
Sporophylls	0.50	narcotic	50
Cystophyllum	0.25	cramp	50
Laminaria	0.50	cramp	40

From the above results, the author thinks that the cod liver oil toxin may be attributed to the alge.

Biochemical Studies of the Locust. (III.)

(pp. 710～712)

By Chikafumi ICHIKAWA.

(The Soma Agricultural and Sericicultual School; Received June 19, 1937.)

Studies on the Wine Yeasts indigenous to Japan.

(pp. 713～735)

By Kinichiro SAKAGUCHI, Sadanobu MORI and Toshio SHIZUME.
(Agricultural Chemical Laboratory, Tokyo Imperial University; Received December 16, 1936.)

Study on the Essential Oil of Black Tea. (Part III.)

(pp. 736～750)

By Ryo YAMAMOTO and Ken ITO.
(Received June 7, 1937.)

1300 kg of Formosan black tea of standard quality were subjected to steam distillation. The distillate was extracted with ether, concentrated, and residual solution was separated by usual method. The following table shows the main components obtained by fractional distillation.

Compounds	Yields (g)
Acids	32.0
Phenols	8.3
Basic substance	0.5
Aldehydes	36.4
Neutral essential oil	173.2

1. Acids.

Acids and phenols were first separated by means of 5% NaOH from original essential oil. The mixture was then treated with sodium bicarbonate, and separated it into each component. Propionic acid was first isolated as p-jod phenacylester, then palmitic acid (20 g) were separated in crystalline form. Steam distillation was next carried out and volatil acid was collected, distillated in vacuum. Yield was 12 g. Isovaleric, n-caproic, hexenic, caprylic acids were isolated as p-jod phenacylester or acid anilid. The main principles in quantity, were caproic and isovaleric acid.

Besides above free acids, caproic acid was found as ester form in the neutral essential oil which distillated in vacuum of 40 mm and 4 mm pressure, and a very little quantity of benzoic acid was also isolated in the former distillate. Both of these acids were supposed to be ester with primaly alcohols such as hexenol n-octanol phenylethyl alcohol and geraniol.

2. Phenols.

From acid solution mentioned above, salicylic acid (3.7 g) was isolated in crystalline form, but it was believed that the acid must be existed, originally, in its methyl ester which has been decomposed by the treatment of alkali and acid in the course of the separation of other ingridients. The

residual phenolic solution was distillated in vacuum of 4 mm pressure, yield was 4.3 g. The main part was distillated at 55～91°/4 mm from which para cresol and the mixture of orth and meta cresol were ascertained as 3.5 dinitrobenzoates.

3. Basic substance.

This was separated by means of 4% H_2SO_4 from residual essential oil. The main part was distillated at 88～95° in vacuum of 40 mm pressure. Yield was 0.2 g. It was identified as quinoline by deriving picrate.

4. Aldehydes.

Aldehyde was next separated by adding sodiumbisulphite and free aldehyde was distillated,

The first in ordinary pressure (I)	B. p. 37～90° Yield 2.5 g
The second in 40 mm pressure (II)	B. p. 35～85° Yield 5.1 g
The third in 4 mm pressure (III)	B. p. 50～85° Yield 3.4 g

The main fraction of No. I was distillated at 70°～90°. Isovaler n-butylaldehyde had been found on previous study (Part II). Present investigation was concerned with the distillates of No. II and No. III. Caproic aldehyde was isolated from the distillates of 35～50°/40 mm and 55～85°/40 mm fractions, benzaldehyde was found in the distillate of 55～60°/4 mm fraction both of them were isolated as 2 : 4 dinitrophenylhydrazone or semicarbazone.

5. Neutral essential oil.

After separated acid, phenol, aldehyde and basic substance, the neutral solution, namely the main part of essential oil, was distillated.

The fractions were ;

Pressure (mm)	Boiling point	Yield (g)
760	41～ 55	16.0
100	30～ 40	9.0
40	32～ 82	22.8
4 (I)	55～ 82	71.8
4 (II)	95～144	35.4

The present investigation was carried on the distillates of 40 mm and 4 mm (I) pressure.

(A) Distillate of 40 mm

i) Sulphur compound.

In distillates of 100 mm, 40 mm, 4 mm (II), fractions and their vapour, escaped from vacuum distillation, collected in the receiver cooled at −60°, a sulphur compound was detected. The reactions of sulphur were most remarkable in the liquid collected at −60°. Although the pure isolation could not succeeded, the experiment was carried on the concentrated solution. It was neutral colorless liquid boiling at 102～112°, but when it has been exposed in the air at room temperature changed to bluish brown color and

finaly depposited to brown black precipitate. The original liquid scented no bad smell, but when it has been reduced with sodium and alcohol in ethereal solution, gave methylmercaptan and an unknown sulphur containing acid having unpleasant smell. The resulted methylmercaptan has been identified as 2,4-dinitrophenylmethyl thioether. The nature of original sulphur compound has not yet been ascertained. But suggesting from reduction products it was supported to be a kind of thiosulphonic methylester. This sulphur compound was also found in black tea and Japanese green tea, so it believes to be a normal ingredient of tea leaves.

ii) Alcohols.

When sulphur compound, caproic, benzoic acid which existed in ester form, have been eliminated by sodium in the distillates of 40 mm pressure, then residual mother liquid gave good flavour. It consisted of hexenol, hexanol, and n-octanol. These primary alcohols were identified as p-Jodphenylurethans.

(B) Distillate of 4 mm

As mentioned on previous paper, distillates of 50～90°/4 mm fractions contained strong good flavour. Phenylethylalcohol, citronellol and geraniol were main constituents of primary alcohols, a part of which was existed in ester form combined with caproic aicd. Experiment has now been carried away as to separate primary and secondary alcohols by the aide of phtalic anhydride and residual essential oil was finaly treated with metalic sodium to get tertiary alcohol and other substances. Linalool was isolated, it was identified as phenylurethan in crystalline form. But on the consequence the unknown substance which gave strong flavour was decomposed. The content of linalool seemed to be comparatively large in quantity in the distillate of 60～75° in 4 mm pressure.

Comparing above results with essential oil of Japanese green tea, benzaldehyde, isovaleric, caproic, caprylic acid, cresol, hexanol, n-octanol, linalool have been isolated by Takei and his co-workers.

Experiment on the Colon Group of Fishes.

(pp. 751～758)

By Yutaka YASUKAWA.

(From the Department of Food Control of the Government Institute from Infectious Diseases. Head of the Department: Dr. Y. Tohyama)

(Received June 10, 1937.)

The colon group, as defined, is a large and complex one including a

number of closely related but distinct species and varieties.

It may be of practical value to distinguish and classify these different types and, if possible, to correlate them with their habitat.

However it is difficult to distinguish and classify the colon group of bacteria from humen feces and the other animals, but I found distinctively the distinguishable point between the colon bacteria isolated from humen feces and intestinal tracts of fishes.

The fish used on these experiments are as follows;

River fish 47, mountain stream fish 48, sea fish 46 (in Bay), 104 (out of Bay) and fishes are all living.

Isolated 61 strains of coli form bacilli from river fish, 56 strains from mountain stream fish, 52 from sea fish in Bay, and 133 from sea fish out of Bay.

Characteristics of Colon Group of these Fishes.

1. Rods.
   0.4 to 0.8 by 1.0 to 4.0 microns, occurring singly and in pairs and occasionally in long chains.
2. The Endo agar.
   These colonies were colorless; but coli colonies from human fece produced a rose color on it.
3. Methyl red and Voges Proskauer's reaction.
   Both reactions are negative. (except river fish strains)
4. Coagulation of Milk.
   All strains becoming alkaline. (except river fish strains)
5. Indol reaction.
   Ehrlich's test was used in the detection of indol.
   Few strains formed it, but are of a low standard. (except river fish strains)
6. Lackmus Molke.
   All strains alkaline. (except river fish strains)
7. Reduction of Neutral Red.
   Few strains reduced it. (except river fish strains)
8. Eijkman's test.
   All strains not formed gas, but few strains formed acid.
9. Fermentation of carbohydrates.
   No acid and gas in lactose, dulcitol especially. (except river fish strains)
10. The resisting power against the heat.

All strains perished within 10 minutes by temperature of 56°C.

11. Growing pH.
In below pH 5.4 is unfit for growth, while sea fish strains is unfit in below pH 5.8 already.

12. Growing power at each concentration of glucose.
No gas formation in the broth over 10% of glucose. (except river fish strains)

13. Optimum temperature.
25~32°C.

14. Growth on the special culture medium.
All strains are unfit for Eosin methylen blue and Simmons' citate agar.

It is possible to draw a clear line between commou B. coli and colon bacteria of fish by the above facts. The river fish strains resembler to the common B. coli than the other fish strains in their characteristics.

I could confirm that the river fish had been polluted with the sewage and any other factors. Therefore we must be employed the fish free from pollution if investigate colon bacteria of fish.